

Controlling the quantum stereodynamics of ultracold bimolecular reactions

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Molecular collisions in the quantum regime represent a new opportunity to explore chemical reactions. Recently, atom-exchange reactions were observed in a trapped ultracold gas of KRb molecules. In an external electric field, these polar molecules can easily be oriented and the exothermic and barrierless bimolecular reactions, $\text{KRb} + \text{KRb} \rightarrow \text{K}_2 + \text{Rb}_2$, occur at a rate that rises steeply with increasing dipole moment. Here we demonstrate the suppression of the bimolecular chemical reaction rate by nearly two orders of magnitude when we use an optical lattice trap to confine the fermionic polar molecules in a quasi-two-dimensional, pancake-like geometry, with the dipoles oriented along the tight confinement direction. With the combination of sufficiently tight confinement and Fermi statistics of the molecules, two polar molecules can approach each other only in a 'side-by-side' collision under repulsive dipole-dipole interactions. The suppression of chemical reactions is a prerequisite for the realization of new molecule-based quantum systems.

Chemical reaction rates often depend strongly on stereodynamics, namely the orientation and movement of molecules in three-dimensional (3D) space^{1–3}. An ultracold molecular gas, with a temperature below 1 μK , provides a highly unusual regime for chemistry, where the motion of two colliding molecules is strictly quantized. Atom-exchange reactions observed in a recent experiment with an ultracold gas of KRb molecules proceed with a single partial wave in the quantum threshold regime⁴. In an external electric field, the reaction rate has a strong dependence on the induced molecular dipole moment⁵. The quantum stereodynamics of the ultracold collisions can be exploited to suppress these bimolecular chemical reactions. We can confine the polar molecules in quasi-2D optical traps, with the molecular dipoles oriented perpendicular to the 2D plane^{6,7}. By precise quantum-state control of both the internal and external degrees of freedom of the molecules, we ensure that two polar molecules can approach each other only in a 'side-by-side' collision, dictated by the Fermi statistics of the molecules and the trap confinement. Chemical reactions are thus suppressed by the repulsive long-range dipole–dipole interaction. The suppression of chemical reactions opens the way for investigation of a dipolar molecular quantum gas. As a result of the strong, long-range character of the dipole–dipole interactions, such a gas brings fundamentally new abilities to quantum-gas-based studies of strongly correlated many-body physics, where quantum phase transitions and new states of matter can emerge^{8–13}.

Two colliding polar molecules interact through long-range dipole–dipole forces well before they reach the shorter distance scales where chemical forces become relevant. Therefore, the spatial anisotropy of the dipolar interaction can play an essential role in the stereochemistry of bimolecular reactions of polar molecules. In general, one expects the attraction between oriented dipoles in a 'head-to-tail' collision to be favourable for chemical reactions, whereas the repulsion between two oriented polar molecules in a 'side-by-side' collision presents an obstacle for reactions.

Up to now, however, large centre-of-mass collision energies have precluded the direct control of chemical reactions through dipolar interactions. In a cold collision regime, where tens of scattering partial waves contribute, one can begin to exert control of intermolecular dynamics through the dipolar effect¹⁴. An ultracold gas, however, provides an optimum environment in which to fully investigate the dipolar effects^{5,15,16}. Here, the molecules can be prepared in identical internal quantum states, with the dipoles oriented using an external electric field, and the molecular gas confined in external potentials created using light. In the limit of vanishing collision energies, the stereodynamics is described by only a few quantized collision channels, and, moreover, for indistinguishable molecules, the states of translational motion are coupled to internal molecular states because the quantum statistics of the molecules (fermions or bosons) dictates a particular symmetry of the total wavefunction with respect to exchange of two molecules. In this quantum regime, we have an opportunity to suppress or enhance reaction rates by understanding and precisely controlling the stereodynamics of colliding polar molecules.

2D versus 3D trapping geometry

The spatial geometry of the confining potential can influence collisions in a trapped dipolar gas. This effect has been explored for elastic collisions of magnetic atoms¹⁷; here, we exploit spatial geometry to control chemical reactions of polar molecules. In particular, a 2D trap geometry, with the dipoles oriented parallel to the tight confinement direction \hat{z} , is well matched to the spatial anisotropy of the dipole–dipole interaction^{18–20}. We can realize such a geometry using a 1D optical lattice (see Fig. 1a), where the trapped molecules are divided among several isolated layers. In each of these layers, the lattice potential provides tight harmonic confinement in \hat{z} such that only the lowest few quantized motional states in \hat{z} are occupied. Consequently, within each isolated layer, colliding molecules approach each other in two dimensions. However, the

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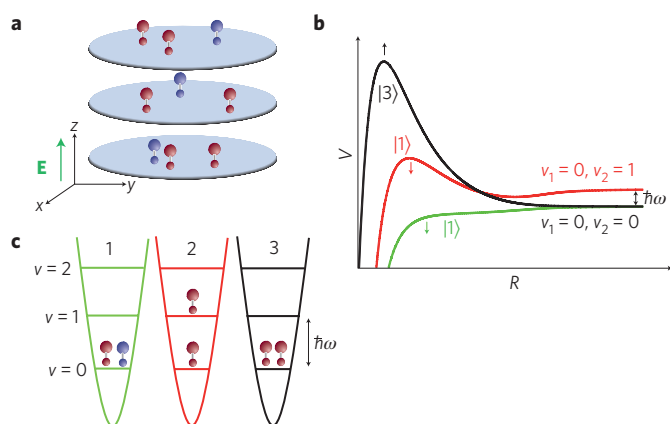


Figure 1 | Quantized stereodynamics of ultracold chemical reactions in quasi-two dimensions. **a**, A quasi-2D geometry for collisions is realized for polar molecules confined in a 1D optical lattice. An external electric field is applied along the tight confinement axis. **b**, Schematic showing the three lowest adiabatic potentials for collisions as a function of the intermolecular separation, R . These three channels are ordered with increasing magnitude of the centrifugal barrier. The arrows indicate the change in the potential for an increasing external electric field, and hence a growing induced dipole moment. **c**, Schematic showing each individual case for the three lowest collision channels. The lowest-energy collision channel occurs when two molecules are prepared in different internal states (indicated here by the colours of the molecules). The second channel is realized when two identical molecules are prepared in different vibrational levels ν for their \hat{z} motions. The third case has a much reduced loss rate as a consequence of an increased centrifugal barrier when the two identical molecules are prepared in the same vibrational level along \hat{z} .

range of the van der Waals interaction (and, for that matter, the range of dipolar interactions at our largest external electric field) is still smaller than the spatial extent of the cloud in the direction of tight confinement, a_{ho} , and, therefore, at short intermolecular distances, a collision still must be treated in three dimensions.

As discussed above, the two-molecule wavefunction must obey an overall symmetry with respect to the exchange of the identical molecules. This couples the internal degrees of freedom of the molecules with their motional degrees of freedom, resulting in a strong modification of the collision process through control of internal states. Exploiting this coupling relies on the fact that ultracold collisions, including ultracold chemical reactions, will be dominated by the allowed collision channel with the lowest centrifugal barrier. In three dimensions, ultracold fermions, such as our molecules, that are spin-polarized (in the same internal state) collide in the partial-wave channel with $L = 1$ (p wave), where $\hbar L$ is the quantized relative angular momentum. Here, $\hbar = h/2\pi$ and h is Planck's constant. On the other hand, fermions in different internal states can collide in s waves ($L = 0$). This behaviour is familiar from the example of ultracold fermionic atoms²¹. For the case of dipoles, the dipole–dipole interaction mixes states with different L , such that one should replace $L = 0$ with the lowest-energy adiabatic channel with even L , which does not have a centrifugal barrier. Similarly, $L = 1$ becomes the odd- L adiabatic channel with the lowest centrifugal barrier. The approach of controlling the relative motion through control of the internal molecular states has a serious limitation, which is that we do not have control over the projection of the relative angular momentum of the colliding particles on the \hat{z} axis, M . This is especially important for dipoles, where M describes whether the dipoles approach ‘side-by-side’ (for example, $L = 1, M = \pm 1$), and therefore experience a repulsive dipole–dipole interaction, or ‘head-to-tail’ (for example, $L = 1, M = 0$), where the dipole–dipole interaction is attractive.

By confining polar molecules in two dimensions, we gain control over M . With extremely strong confinement and large dipole moments oriented perpendicular to the 2D plane, one could, in principle, achieve a fully 2D geometry where the molecules could approach each other only side-by-side (odd M) simply because of the repulsive part of the dipole–dipole interaction^{6,7}. Alternatively, in our present experimental situation of quasi-2D trapping, we can again use the overall symmetry of the two-molecule wavefunction for fermionic molecules to control M . In quasi-two dimensions, L is no longer a good quantum number for describing how molecules approach each other at intermolecular separations that are much larger than a_{ho} ; instead, the relative motion is described by M . In addition, we have a new (compared with the 3D case) quantum number that describes the harmonic oscillator motional state in z for each molecule. This quantum number, which we label ν , acts as a new internal degree of freedom for the molecules as they approach each other in the long range, in the sense that we can relatively easily control the occupation in the different ν states and this will in turn give us control over the relative motion described by M . Specifically, fermionic molecules in the same internal state and the same ν must collide with odd M , whereas fermions in the same internal state but different ν can collide with even M .

Stereodynamics and quantized collision channels

We now consider the quantized collision channels that define the stereodynamics in this quasi-2D geometry. We identify three collision channels relevant to the stereodynamics, and we label these |1>, |2> and |3>, in order of increasing centrifugal barrier heights. Figure 1b shows schematically the adiabatic potentials for these three lowest-energy collision channels. Collision channel |1> corresponds to spatially isotropic collisions, collision channel |2> is the quantum analogue of ‘head-to-tail’ collisions, and collision channel |3> is the quantum analogue of ‘side-by-side’ collisions (further details are provided in the Methods section). Channels |1> and |2> become increasingly favourable for chemical reactions as the dipole–dipole interaction strength is increased, for example by increasing the external electric field E . In contrast, channel |3> has a centrifugal barrier whose height increases for higher dipole moment, within the $|E|$ range considered in this work. This barrier hence continues to prevent molecules from reaching short range.

Figure 1c shows how these different collision channels can be accessed through control of the internal molecular states and the \hat{z} motional states. In Fig. 1c, molecules in different internal states are shown in different colours and the harmonic oscillator states in \hat{z} are labelled by ν . In case (1), for two molecules in different internal molecular states and in any combination of ν levels, channel |1> is allowed, resulting in no centrifugal barrier. In case (2), when the molecules are prepared in identical internal molecular states but in different ν levels, the lowest-energy collision channel is |2> (‘head-to-tail’). In case (3), where the molecules are prepared in the same internal state and the same ν level, the two lower-energy collision channels are no longer allowed, and reactions can proceed only through channel |3> (‘side-by-side’). This case is the least favourable for atom-exchange bimolecular chemical reactions and thus results in a strong suppression of inelastic losses in the molecular sample.

Preparation of the 2D molecular system

We create a trapped, ultracold gas of $^{40}\text{K}^{87}\text{Rb}$ molecules, in their lowest-energy rovibrational level and in a single hyperfine state²², following the techniques described in ref. 23. To confine the molecules, we start with a crossed-beam optical dipole trap, with a harmonic trapping frequency of 180 Hz along the vertical direction (\hat{z}) and 25 Hz in the transverse directions. For the present work, we add an optical lattice along \hat{z} , which is formed by a retro-reflected beam with a $1/e^2$ waist of 250 μm and a wavelength of 1,064 nm. Both optical dipole trap beams and the optical lattice beam are linearly polarized and their polarizations are mutually

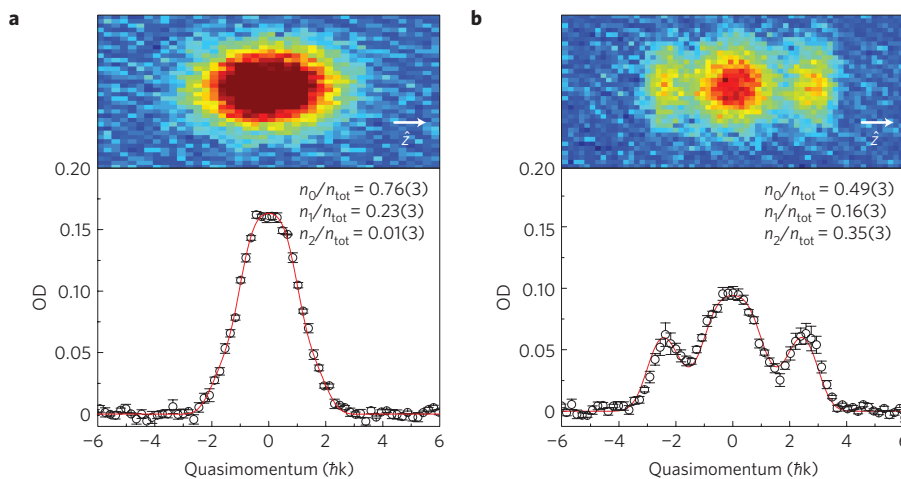


Figure 2 | Relative population of molecules in the lattice vibrational levels. We measure the relative population in each lattice vibrational level using a band-mapping technique. **a, b.** The results for the initial distribution of molecules (**a**) and for a non-thermal distribution created by parametric heating in \hat{z} (**b**). The two images use the same colour scale for the optical depth (OD). The images are an average of five shots (**a**) and seven shots (**b**), taken after 10 ms of free expansion. Below each image we show a trace along \hat{z} that corresponds to the OD averaged over the transverse direction. A fit (red line) to the trace, which takes into account both the size of the Brillouin zones and our imaging resolution, is used to extract the relative populations, n_ν/n_{tot} , in each lattice level ν . The horizontal axis corresponds to momentum in \hat{z} and is marked in units of the lattice momentum $\hbar k$, where k is the lattice wave vector. Error bars represent one standard deviation (s.d.).

orthogonal. Each layer of the optical lattice trap is tightly confining in \hat{z} with a harmonic trapping frequency of $\nu_z = 23$ kHz for the molecules, whereas in the transverse directions, the combined trap has a harmonic trapping frequency of 36 Hz. The tunnelling rate between lattice layers is negligible and, therefore, each layer realizes an isolated trap for the molecules. Initially, 34,000 ground-state molecules are confined in roughly 23 layers, with the centre layer having 2,200 molecules and a peak density of $3.4 \times 10^7 \text{ cm}^{-2}$.

We start by loading ultracold ^{40}K and ^{87}Rb atoms from the crossed-beam dipole trap into the combined trap by turning up the intensity of the optical lattice beam in 150 ms. We then create molecules in the lattice by first forming extremely weakly bound molecules through magneto-association of atom pairs and then coherently transferring these molecules into their rovibrational ground state using optical transitions²³. The temperature of the molecular gas, T , in the combined optical dipole plus lattice trap can be varied between 500 and 800 nK by varying the initial atom gas conditions. To completely freeze out the motion of the molecules along \hat{z} requires that $k_B T \ll \hbar \nu_z$, where k_B is Boltzmann's constant. For a gas at $T = 800$ nK in our lattice, $k_B T / \hbar \nu_z = 0.72$ and we expect 25% of the molecules will occupy higher ν levels.

As discussed above, to control the stereochemistry of bimolecular reactions in the ultracold gas, we need to control both the internal state and the harmonic oscillator level ν of the molecules. We create the molecules in a single internal quantum state. If desired, we can subsequently create a 50/50 mixture of molecules in the ground and the first excited rotational states by applying a resonant microwave $\pi/2$ -pulse²². The occupation of lattice levels ν can be controlled by varying T ; alternatively, we can prepare a non-thermal distribution of molecules using parametric heating. Here, the lattice intensity is modulated at twice ν_z , and, as a result, molecules initially in the $\nu = 0$ level are excited to the $\nu = 2$ level.

We determine the population in each lattice level using an adiabatic band-mapping technique^{24,25}. As the lattice potential is ramped down slowly, molecules in different vibrational levels of the lattice are mapped onto Brillouin zones. The measured molecule momentum distribution following this ramp is shown in Fig. 2a for a $T = 800$ nK molecular gas. The measured fraction in $\nu = 0$ matches well with the expected thermal distribution. In contrast, Fig. 2b shows the measured non-equilibrium occupation of lattice vibrational levels following parametric heating.

Measurement of molecular loss rates

We measure the bimolecular reaction rate by monitoring the loss of trapped molecules as a function of time. To image the molecules, we reverse our coherent transfer process to bring the molecules back to a weakly bound state where we can detect the molecules with time-of-flight absorption imaging²³. The molecules are imaged after free expansion from the combined optical dipole plus lattice trap. From the images, we obtain the total number of molecules and the radial cloud size. As we do not resolve the individual layers of the optical lattice, we obtain an average 2D density per layer by dividing the total number by the cross-sectional area of the cloud, and by an effective number of layers α , as defined in the Methods section.

In Fig. 3a, we show the average 2D density as a function of time. For these data, the molecules are all prepared in the same internal state and $|E|$ is 4 kV cm^{-1} , which gives an induced molecular dipole moment in the laboratory frame of 0.158 Debye (D), where $1 \text{ D} = 3.336 \times 10^{-30} \text{ C m}$. The two data sets in Fig. 3a correspond to an unperturbed $T = 800$ nK gas (black squares) and a parametrically heated gas (red circles). For the case where parametric heating was used to increase population in $\nu > 0$ levels, the data show a faster initial loss of molecules. This indicates that the initial loss is predominately due to interlevel collisions as described in case (2) of Fig. 1c, whereas intralevel collisions (case (3) of Fig. 1c) give a slower loss of molecules at longer times.

We fit the data using a simple model, which assumes two loss-rate constants: one for interlevel collisions, $\beta_{(2)}$, and a second one for intralevel collisions, $\beta_{(3)}$ (with the subscripts referring to the adiabatic channels labelled in Fig. 1b). Here,

$$\begin{aligned} \frac{dn_0}{dt} &= -\beta_{(3)} n_0^2 - \beta_{(2)} n_0 n_1 - \beta_{(2)} n_0 n_2 \\ \frac{dn_1}{dt} &= -\beta_{(2)} n_0 n_1 - \beta_{(3)} n_1^2 - \beta_{(2)} n_1 n_2 \\ \frac{dn_2}{dt} &= -\beta_{(2)} n_0 n_2 - \beta_{(2)} n_1 n_2 - \beta_{(3)} n_2^2 \end{aligned} \quad (1)$$

where n_ν is the 2D density of molecules in a particular lattice vibrational level ν . To fit the measured time dependence of the total

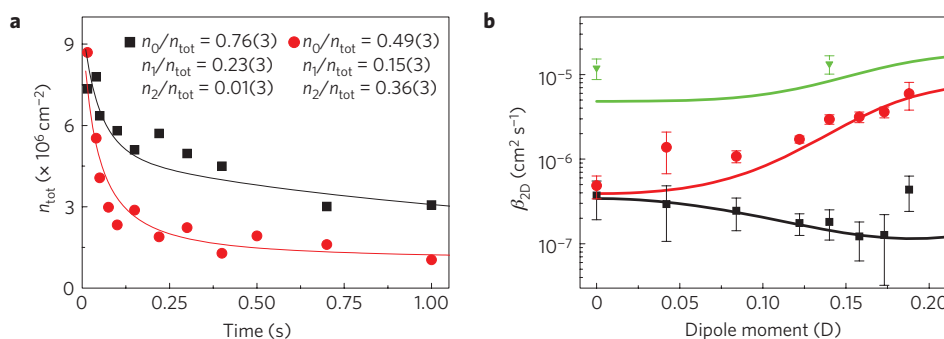


Figure 3 | Measurements of 2D loss rates and comparison with theory. a, A fit (solid lines) to the measured loss curves, with (red circles) and without (black squares) 0.3 ms of parametric heating in \hat{z} , is used to extract the loss-rate constants $\beta_{|3\rangle}$ and $\beta_{|2\rangle}$. **b**, The extracted loss-rate constants for collisions of molecules in the same lattice vibrational level (black squares) and from different lattice vibrational levels (red circles) plotted for several dipole moments. Measured loss-rate constants for molecules prepared in different internal states are shown as green triangles. Error bars represent 1 s.d. For comparison with each of these three measurements, we include a quantum scattering calculation for $\nu_z = 23 \text{ kHz}$, $T = 800 \text{ nK}$ (solid lines). The potentials corresponding to the dominant loss channel for the three cases are shown in matching colours in Fig. 1b,c.

2D density, $n_{\text{tot}}(t)$, we use $n_{\text{tot}}(t) = n_0(t) + n_1(t) + n_2(t)$. We input the measured initial populations n_ν/n_{tot} (see Fig. 2 and the Methods section) at $t = 0$, and we fit the data to the numerical solution of equation (1). We obtain $\beta_{|3\rangle}$ and $\beta_{|2\rangle}$ from a simultaneous fit to the two measured $n_{\text{tot}}(t)$ curves shown in Fig. 3a.

By repeating this procedure for different values of $|\mathbf{E}|$, we measure the chemical reaction rate constants, $\beta_{|3\rangle}$ and $\beta_{|2\rangle}$, as a function of the induced dipole moment. In Fig. 3b, we show the intralevel (black squares) and interlevel (red circles) chemical rate constants as a function of the dipole moment. Also shown as green triangles in Fig. 3b are the results of two measurements for a 50/50 mixture of molecules in different rotational states (case (1) of Fig. 1c). Here, we fit the loss of molecules in the ground rotational state to the solution of $(dn_{\text{tot}}/dt) = -\beta_{|1\rangle}n_{\text{tot}}^2$ to extract a single loss-rate constant.

Experiment–theory comparison

For comparison with these measurements, we carry out quantum scattering calculations using a time-independent quantum formalism based on spherical coordinates with cylindrical asymptotic matching to describe the molecular collisions in quasi-two dimensions²⁶. We use an absorbing potential at short distance to represent chemical reactions^{19,27}. This technique showed excellent agreement with previous experimental data for KRb bimolecular reactions in three dimensions^{4,5}. We computed the loss-rate coefficients β_{ν_1, ν_2} for molecules in different initial lattice vibrational states ν_1, ν_2 , at a collision energy of 800 nK. When the induced dipole moment is still small (0–0.2 D), the measured temperature is a good approximation for the mean collision energy. The loss rates of the different processes can be separated into fast loss rates ($\beta_{0,1}, \beta_{0,2}, \beta_{1,2} \approx \beta_{|2\rangle}$) and slow loss rates ($\beta_{0,0}, \beta_{1,1}, \beta_{2,2} \approx \beta_{|3\rangle}$). The black theoretical curve in Fig. 3b corresponds to an average of the slow rates weighted by the initial populations n_0, n_1, n_2 . The red curve corresponds to the same average, but for the fast rates. The green curve corresponds to the loss rate of molecules in different internal states.

The three measured reaction rate constants shown in Fig. 3b are consistent with the quantum scattering calculations for the collision channels shown in matching colours in Fig. 1b,c. Molecules in different rotational states (green triangles in Fig. 3b) have the highest rate for chemical reactions, consistent with the fact that they can collide in channel |1>, which corresponds to spatially isotropic collisions with no centrifugal barrier. On the other hand, molecules prepared in the same internal molecular state (red circles and black squares in Fig. 3b) have suppressed reaction rates because the lowest-energy collision channel is

no longer allowed. Instead, identical molecules in different lattice levels (red circles in Fig. 3b) react predominantly through collisions in channel |2>, or ‘head-to-tail’, whereas identical molecules in the same lattice level (black squares in Fig. 3b) react through collisions in channel |3>, or ‘side-by-side’. The importance of stereodynamics on the reaction rate for polar molecules is manifest in the very different dipole-moment dependence of the reaction rates in these two collision channels. In particular, for the case where the molecules are prepared both in the same internal quantum state and in the same ν level, the reaction rate is suppressed even as the dipole moment is increased.

2D versus 3D loss rates

Figure 4 shows how the initial loss rate in a gas of identical molecules depends on the fractional occupation of the lowest lattice level, n_0/n_{tot} . As n_0/n_{tot} increases, the calculated initial loss-rate constant for a molecular gas in thermal equilibrium (solid black line) changes from close to $\beta_{|2\rangle}$ (the red line indicating the measured value at 0.174 D from Fig. 3b) to $\beta_{|3\rangle}$ (open symbol at $n_0/n_{\text{tot}} = 1$). In thermal equilibrium, the fractional occupation of the lowest vibrational level is given by the Boltzmann distribution (see the Methods section). On the top axis of Fig. 4, we give the corresponding values of the scaled temperature ($k_B T/h\nu_z$). The filled triangles in Fig. 4 correspond to the measured initial loss rate at different temperatures (500 nK and 800 nK), and the open symbol at $n_0/n_{\text{tot}} \approx 0.5$ corresponds to the initial loss rate for the parametrically heated, non-thermal molecular gas.

We also directly compare the suppressed chemical reaction rate in quasi-two dimensions with that of the 3D case in the inset to Fig. 4. Here, we compare data for a 3D geometry from ref. 5 against the suppressed loss-rate constant measured in quasi-two dimensions. For the comparison, the 2D loss rate is scaled to three dimensions using $\beta_{3D} = \sqrt{\pi} a_{\text{ho}} \beta_{2D}$ (refs 20,28,29), where a_{ho} is the harmonic oscillator length in \hat{z} . For a dipole moment d greater than 0.1 D, the 3D loss-rate constant increases markedly as d^6 (refs 5,30), whereas the scaled loss-rate constant for the quasi-2D case remains close to the value at zero electric field. At a dipole moment of 0.174 D, the measured suppression in quasi-two dimensions is a factor of 60.

Outlook

The results shown here demonstrate how quantum stereochemistry in the ultracold regime can be used to control reaction rates. The capability of precisely controlling the molecular quantum states for both the internal and external degrees of freedom is

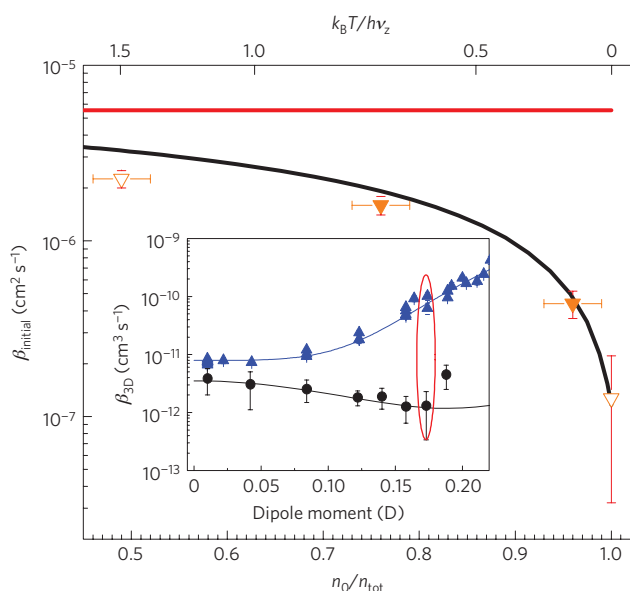


Figure 4 | Loss rates from three dimensions to two dimensions. The effective initial loss rate, β_{initial} , for polar molecules confined in a 2D geometry depends on the fractional population (n_0/n_{tot}) in the lowest harmonic oscillator level in \hat{z} , which for a gas in thermal equilibrium depends on the ratio $k_B T/h\nu_z$. The measured initial loss rates for a dipole moment of 0.174 D are shown for two different thermal distributions (solid triangles), a non-thermal sample created by parametric heating (the top open triangle) and an extracted pure $\beta_{3|3}$ for the limit of the entire population residing in the lattice ground vibrational level (the bottom open triangle). The experimental results agree well with a simple model (black curve) described in the text and the Methods section. The top line indicates the value of $\beta_{2|2}$ as given in Fig. 3b. Inset: The extracted intralevel loss rate for identical fermionic KRb molecules in two dimensions (black circles) compared with the loss rate in three dimensions (blue triangles). The 3D data for $T = 300$ nK are from ref. 5. The 2D data were taken at $T = 800$ nK and are converted to 3D rates by multiplication with $\sqrt{\pi} a_{\text{ho}}$, where a_{ho} is the harmonic oscillator length in \hat{z} . The red oval highlights the data for a dipole moment of 0.174 D. Error bars represent 1 s.d.

a key ingredient for this advance. The strong suppression of reaction rates for a gas of fermionic molecules in a quasi-2D geometry opens the door for creating a stable ultracold gas of polar molecules and studying the many-body physics of such a system. Whereas a future, alternative possibility is to produce an ultracold gas of a bialkali molecular species that might be stable against bimolecular chemical reactions (although it is an open question with respect to three-body losses)^{31–33}, the approach we demonstrate here is appealing considering that a number of bialkali polar molecular species under study at present are expected to experience chemical reactions at rates similar to the KRb case^{20,31–33}.

Methods

The low-energy collision channels [1], [2] and [3] can be labelled with four relevant quantum numbers, η, L, γ and M . The quantum number γ identifies the exchange symmetry of the part of the two-molecule wavefunction that describes the relative motion in \hat{z} ; for the symmetric case, $\gamma = 1$, and for the antisymmetric case, $\gamma = -1$. For two molecules in the same \hat{z} harmonic oscillator state, $\gamma = 1$, whereas both $\gamma = 1$ and $\gamma = -1$ are possible for two molecules in different harmonic oscillator states. Similarly, we use a quantum number η to keep track of the exchange symmetry of the part of the wavefunction that describes the internal states of the two molecules. For two molecules in the same internal quantum state, $\eta = 1$, whereas $\eta = \pm 1$ for molecules in different internal states. In two dimensions, three quantum numbers (M, γ, η) are sufficient to describe the quantum stereodynamics. However, because the interactions at short range must be described in three dimensions, the quantum number corresponding to the 3D

angular momentum, L , as well as M , becomes relevant. With collisional channels described by quantum numbers η, L, γ and M , the fermionic symmetry can be concisely stated in the following relations:

$$\eta(-1)^L = -1, \quad \text{short range, 3D}$$

$$\eta\gamma(-1)^M = -1, \quad \text{long range, 2D}$$

Collision channel [1] has $\eta = -1, L = 0, \gamma = 1$ and $M = 0$, and corresponds to spatially isotropic collisions. Collision channel [2] has $\eta = 1, L = 1, \gamma = -1$ and $M = 0$, and is the quantum analogue of ‘head-to-tail’ collisions. Collision channel [3] has $\eta = 1, L = 1, \gamma = 1$ and $M = \pm 1$, and is the quantum analogue of ‘side-by-side’ collisions. The dipole–dipole interaction mixes states with different L . However, for convenience, we have denoted the lowest-energy adiabatic channel, which does not have a centrifugal barrier, as $L = 0$. Similarly, $L = 1$ denotes the odd- L adiabatic channel with the lowest centrifugal barrier.

The traces in Fig. 2 were obtained by averaging the images in the transverse direction within one r.m.s. width of the Gaussian distribution. We fit the traces to the convolution of a series of step functions and a Gaussian: the former describes the first three Brillouin zones, whereas the latter characterizes the effect of a finite imaging resolution. The uncertainty in the relative population is 3%, and is dominated by systematic errors arising from the variation of the imaging resolution within the range of 1–2 pixels. We note that after the creation of ground-state molecules, the gas may be slightly out of thermal equilibrium owing to a slight difference in the optical trapping potential between Feshbach and ground-state molecules³⁴.

The average 2D density shown in Fig. 3a is obtained by dividing the total number of molecules, N , by an effective area, $4\pi\alpha\sigma_r^2$, where σ_r is the r.m.s. cloud size in the transverse direction and N/α is a number-weighted average over the occupied lattice layers. We calculate $\alpha(t=0) = 23$ assuming an initial discrete Gaussian distribution in \hat{z} with an r.m.s. width that we measure after transferring the molecules back to the optical dipole trap. However, α increases at longer times because of the density dependence of the loss. For our analysis, we use a time-averaged value $\alpha = 30$ that was determined by comparing an analysis based on a uniform layer density with a numerical simulation of the loss in each layer. The uncertainties for $\beta_{3|3}$ and $\beta_{2|2}$ are dominated by statistical uncertainties in the fits to $n_{\text{tot}}(t)$. For the data shown in green triangles in Fig. 3b, the two internal molecular states are $|0, 0, -4, 1/2\rangle$ and $|1, 1, -4, 1/2\rangle$, following the notation of ref. 22.

For the solid black line in Fig. 4, the fractional molecular population $f(\nu, T)$ in a vibrational level ν at temperature T is obtained from a Boltzmann distribution, and the effective β_{initial} is then calculated as

$$\beta_{\text{initial}} = \beta_{3|3} \sum_{\nu} f(\nu, T)^2 + \beta_{2|2} \sum_{\nu_1 \neq \nu_2} f(\nu_1, T) f(\nu_2, T)$$

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Author contributions

The experimental work and data analysis were carried out by M.H.G.d.M., A.C., B.N., D.W., S.O., J.Y. and D.S.J. Theoretical calculations of the inelastic loss rates in the 2D trap were done by G.Q. and J.L.B.

Additional information

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